THE EFFECT OF NEUTRAL SALTS ON THE HYDROLYSIS OF COPPER SULFATE

A THESIS

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BY

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THE EFFECT OF NEUTRAL SALTS ON THE HYDROLYSIS OF COPPER SULFATE

I. INTRODUCTION

The effect of neutral salts on various types of chemical equilibria has been studied by many investigators. However, little work has been devoted to the salt effect on hydrolysis. In those few cases, the investigations have been limited to esters. Thus, it appears that this is the first investigation of neutral salt action on the hydrolysis of an inorganic salt.

There are many methods for determining the degree of hydrolysis; of these, the most widely used are:

(a) Measurement of the catalytic effect of the $H^{'}$ or OH^{-} ion: for example, in the hydrolysis of an ester or the rate of inversion of cane sugar.

Ley, Z. phys. Chem., 30, 193(1899).

Bredig and Fraenkel, Z. Elektrochem., 11, 525(1905).

Kellogg, J. A. C. S., 31, 403,886(1909).

(b) Distribution measurements:

Kahlenburg, Davis and Fowler, J. A. C. S., 21, 1(1894).

(c) Freezing point lowering measurements:

Bredig, Z. phys. Chem., 13, 289(1894).

Göbel, Z. phys. Chem., 89, 49(1914).

(d) Electrical conductivity measurements:

Lunden, Jour. Chem. Phys., 5, 145(1907).

Walker and Aston, J. C. S., 67, 576(1895).

None of the above methods are satisfactory for measuring low concentrations of hydrogen ions.

In the measurement of the hydrolysis of a salt of a weak base and strong acid it is necessary to have a method capable of measuring low concentrations of hydrogen ions. An electrometric method serves this purpose well.

2. HISTORICAL

Denham

H. G. Denham, J. C. S., 93, 41-63(1908).

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using an electrometric method with a hydrogen electrode determined the degree of hydrolysis of a number of different salts and obtained excellent results in many cases. His method had the disadvantages that it could not be used in solutions of salts of metals less noble than hydrogen, in the case of multivalent cations, such as, Fe^{+++}, which are reduced by hydrogen to cations of smaller electrovalency, nor is the method applicable to solutions of salts with reducible anions, such as, NO_3^- and ClO_3^-.

Denham did not investigate the effect of neutral salts since he thought they interfered with the measurement of hydrolysis.

Manning

A. B. Manning, J. C. S., 119, 2079-87(1921).

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studied the rate of hydrolysis of ethyl formate in water alone and in the presence sucrose, glucose, KCl, NaCl, KNO_3, $NaNO_3$, $CaCl_2$, $BaCl_2$, and K_2SO_4. "The values obtained for the velocity constant show that the non-electrolytes exert little or no influence on the rate of hydrolysis, from which it is concluded that the reaction is independent of changes in concentration of the water, that is, hydration of the solute does not affect the velocity constant. The presence of K_2SO_4 decreases the velocity constant about 20% below the value obtained in water alone; while the other salts bring about a marked increase in the value of the constant." The increase was in the order: KNO_3, $NaNO_3$, KCl, NaCl, $BaCl_2$, $CaCl_2$.

He attempted to calculate what this effect should be according to the mixture law of Arrhenius, but the calculated results were so far from those actually obtained that he decided that a new law or some modification of Arrhenius' mixture law was necessary.

Poma and Albonico

G. Poma and G. Albonico, Atti accad. Lincei, 24, I, 747(1915).

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studied the effect of neutral salts on the hydrolysis of methyl acetate and found that neutral salts accelerated the rate and increased the degree of hydrolysis. The increase was in the order of K, Na, Li, and iodides, nitrates, bromides, and chlorides.

The limitations of the hydrogen electrode prevented the determination of the hydrolysis of copper sulfate solutions by an electrometric method until other electrodes were discovered. The quinhydrone electrode is free from the limitations of the hydrogen half-cell and may be used for measuring the hydrolysis of copper sulfate solutions.

O'Sullivan

J. B. O'Sullivan, Trans. Faraday Society, 21, 319(1925).

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determined the hydrolysis of 0.1 N $CuSO_4$ by an electrometric method in which he used a quinhydrone electrode.

The results which he obtained are not to relied upon, as his measurements on four solutions of identical concentration vary as much as 3.5 millivolts. An increase of E.M.F. with time is also noted. These erratic results may be due to possible oxidation of the quinhydrone, since the measurements extend over a period of two days. Also, there is a possibility of diffusion of KCl from the salt bridge into the solution in this prolonged measurement, resulting in an increase of E.M.F.

O'Sullivan did not investigate the neutral salt effect on the hydrolysis of $CuSO_4$.

3. PREPARATION AND PURIFICATION OF MATERIALS

All salts used in this investigation were of C. P. grade and were very carefully purified by recrystallizations from water. In all operations, freshly distilled water was used. The water was boiled immediately before use to expel the dissolved gases.

The purified salts were dried in an oven at 110°C. for a period of 12 hours. The dry salts were put in glass stoppered bottles and kept in a dessicator.

Copper Sulfate

This salt in the form of C. P. $CuSO_4.5H_2O$ was recrystallized three times but was not dried due to the variability in the water of crystallization in the neighborhood of the drying temperature.

The $CuSO_4$ solutions were prepared from the purified salt, standardized by thiosulfate and checked by electrolysis. The two methods agreed by one part in one thousand.

Potassium Chloride, Potassium Sulfate, Sodium Chloride, and Sodium Sulfate

These neutral salts were recrystallized twice from water, except the potassium chloride for use in the calomel electrodes which was recrystallized three times. The NaCl was precipitated from a saturated solution by means of HCl gas since the difference in the solubility of NaCl in hot and cold saturated solutions is insufficient to cause any appreciable amount to crystallize upon cooling the solution. This necessitated longer drying at about 140°C. to free the salt from HCl incorporated in the crystals.

Quinhydrone

The quinhydrone was the standard Eastman product and was not further purified.

Agar-agar Gel

This gel was prepared by soaking two or three grams of agar-agar in water over night, draining and stirring it into about 100c.c. of saturated KCl heated to about 60°C. until throughly mixed. It was found that if the solution was boiled, the gel did not harden properly.

The best grades of C. P. mercurous chloride and redistilled mercury were used for preparing the calomel electrodes.

4. APPARATUS

The saturated calomel electrodes were prepared in the usual manner and checked by means of a carefully standardized 0.1 N HCl solution according to Clark

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W. M. Clark, "Determination of Hydrogen Ions", page 420 3rd. Edition, (Williams and Wilkins, Co.)

The various electrodes used checked within 0.0003 volts.

The salt bridges were prepared by filling a glass tube in the shape of an inverted U with the hot agar gel solution containing KCl and allowing to solidify. Care was taken to prevent the inclusion of air bubbles in the salt bridge as they offer a high resistance to the passage of electric current which results in inaccurate potentials.

Platinum electrodes were made by sealing bright platinum wires in glass tubes and connecting to copper wires by mercury.

A Leeds and Northrup Student's Potentiometer was used for measuring the E.M.F. of the cells. A Leeds and Northrup Wall Type Galvanometer was used as the null instrument.

The standard of electromotive force was a Weston cell which gave an E.M.F. of 1.0182 volts at 20°C.

A lead storage battery was used as the source of opposing E.M.F. since its potential remains more nearly constant than ordinary dry cells.

The constant temperature bath consisted of a large container filled with water maintained at $25^\circ \pm 0.01^\circ C$. The temperature was controlled by a metastatic thermo-regulator. The water was heated electrically and circulation was effected by means of a motor driven stirrer.

5. METHOD AND PROCEDURE

An electrometric method using the quinhydrone electrode was employed for measuring the hydrogen ion concentration, from which the degree of hydrolysis was calculated. The saturated calomel electrode was used as the reference electrode. The liquid junction potentials were practically eliminated by salt bridges of saturated KCl in agar gel solution to retard the diffusion of KCl.

Two complete cells were employed so as to obtain duplicate readings and furnish a means of checking the reproducibility of the cells.

The cell arrangement was as follows:

$$\mathrm{Pt}\left|\begin{array}{l}\text{Quinhydrone}\\ CuSO_4\ (x\ M)\\ \text{Neutral Salt}(y\ M)\end{array}\right|\ KCl(\text{sat.})\ \Big|\ KCl(\text{sat.}), HgCl,\ Hg.$$

The salt solution was placed in the quinhydrone electrode vessel and a sufficient amount of solid quinhydrone added to saturate the solution at 25°C. The set-up as indicated was placed in the bath and allowed to reach the temperature of the thermostat before measurements were taken. Measurements were repeated over intervals of 2 to 4 minutes for a period of 10 to 30 minutes depending upon the constancy of the readings. If the measurements extended over a longer period than 30 minutes (and sometimes less) they were found to deviate from the mean, usually characterized by an increase of potential. The cause of this is probably due to diffusion of KCl from the salt bridge; or possibly to oxidation of the quinhydrone.

At the conclusion of each measurement, the platinum electrode and salt bridge were removed from the solution, washed in distilled water and dried by wiping with absorbent cotton.

At the end of each day the platinum electrodes were cleaned by dipping in a 1:1 mixture of HNO_3 which was heated to boiling for several minutes, washed with dilute NH_4OH and finally with distilled water. They were kept in distilled water while not in use.

The KCl solution in the calomel electrodes was flushed from the cell about every two weeks.

In the course of measurements, the lead storage battery was checked against the standard cell to determine any variation in its potential.

6. CALCULATIONS

The following formula was used for calculating the pH value of the solutions, where V refers to the potentiometer reading,

$$pH = \frac{0.4534 - V}{0.0591}$$

The hydrogen ion concentration(C_H) was calculated by means of the following relationship:

$$- \log C_H = pH$$

The degree of hydrolysis, x, was obtained by substitution in the following, where M refers to the molar concentration,

$$x = \frac{C_H}{2M}$$

7. EXPERIMENTAL RESULTS

Each of the following results represents an independent measurement of a cell and is an average of not less than three readings.

Table 1
No neutral salt present

Molality of $CuSO_4$	E.M.F.	pH	log C_H	$x \cdot 10^4$
0.1000	0.2181			
0.1000	0.2183			
0.1000	0.2177			
	0.2180	3.9818	$\bar{4}.0182$	5.214
0.0500	0.2020			
0.0500	0.2020			
0.0500	0.2022			
0.0500	0.2019			
	0.2020	4.2525	$\bar{5}.7475$	5.591
0.0375	0.1986			
0.0375	0.1989			
	0.1988	4.3075	$\bar{5}.6925$	6.569
0.0250	0.1940			
0.0250	0.1943			
	0.1942	4.3852	$\bar{5}.6148$	8.238
0.0188	0.1906			
0.0188	0.1907			
0.0188	0.1905			
0.0188	0.1903			
	0.1905	4.4469	$\bar{5}.5531$	9.530
0.0125	0.1878			
0.0125	0.1880			
0.0125	0.1877			
0.0125	0.1877			
	0.1878	4.4926	$\bar{5}.5074$	12.870

Table 2
Neutral salt: 1.0N NaCl

Molality of $CuSO_4$	E.M.F.	pH	$\log C_H$	$x \cdot 10^2$
0.0500	0.2964			
0.0500	0.2964			
0.0500	0.2965			
0.0500	0.2965			
	0.2965	2.6540	$\bar{3}.3460$	2.218
0.0375	0.2947			
0.0375	0.2948			
0.0375	0.2948			
0.0375	0.2948			
	0.2946	2.6861	$\bar{3}.3139$	2.747
0.0250	0.2923			
0.0250	0.2923			
	0.2923	2.7250	$\bar{3}.2750$	3.767
0.0188	0.2901			
0.0188	0.2902			
0.0188	0.2895			
0.0188	0.2895			
	0.2898	2.7673	$\bar{3}.2327$	4.557
0.0125	0.2874			
0.0125	0.2875			
	0.2875	2.8062	$\bar{3}.1938$	6.250

Table 3
Neutral salt: 0.75 N NaCl

Molality of $CuSO_4$	E.M.F.	pH	log C_H	$x \cdot 10^2$
0.0500	0.2861			
0.0500	0.2861			
	0.2861	2.8299	$\bar{3}.1701$	1.479
0.0375	0.2847			
0.0375	0.2843			
	0.2845	2.8569	$\bar{3}.1431$	1.854
0.0250	0.2816			
0.0250	0.2817			
	0.2817	2.9043	$\bar{3}.0957$	2.493
0.0188	0.2795			
0.0188	0.2788			
	0.2792	2.9466	$\bar{3}.0534$	3.016
0.0125	0.2744			
0.0125	0.2740			
	0.2742	3.0311	$\bar{4}.9689$	3.724

Table 4
Neutral salt: 0.50 N NaCl

Molality of $CuSO_4$	E.M.F.	pH	log C_H	$x \cdot 10^2$
0.0500	0.2728			
0.0500	0.2724			
	0.2726	3.0582	$\bar{4}.9418$	0.875
0.0375	0.2714			
0.0375	0.2717			
	0.2716	3.0751	$\bar{4}.9249$	1.122
0.0250	0.2701			
0.0250	0.2702			
	0.2702	3.0989	$\bar{4}.9011$	1.593
0.0188	0.2669			
0.0188	0.2662			
	0.2666	3.1597	$\bar{4}.8403$	1.846
0.0125	0.2625			
0.0125	0.2623			
	0.2624	3.2307	$\bar{4}.7693$	2.351

Table 5
Neutral salt: 0.25 N NaCl

Molality of $CuSO_4$	E.M.F.	pH	$\log C_H$	$x \cdot 10^2$
0.0500	0.2544			
0.0500	0.2542			
	0.2543	3.3678	$\bar{4}.6322$	0.429
0.0375	0.2531			
0.0375	0.2534			
	0.2533	3.3847	$\bar{4}.6153$	0.549
0.0250	0.2497			
0.0250	0.2500			
	0.2499	3.4422	$\bar{4}.5578$	0.722
0.0188	0.2483			
0.0188	0.2494			
	0.2489	3.4591	$\bar{4}.5409$	0.927
0.0125	0.2465			
0.0125	0.2460			
	0.2463	3.5031	$\bar{4}.4969$	1.256

Table 6
Neutral salt: 1.0 N KCl

Molality of $CuSO_4$	E.M.F.	pH	$\log C_H$	$x \cdot 10^2$
0.0500	0.2871			
0.0500	0.2871			
	0.2871	2.8129	$\bar{3}.1871$	1.538
0.0375	0.2840			
0.0375	0.2840			
	0.2840	2.8660	$\bar{3}.1340$	1.815
0.0250	0.2799			
0.0250	0.2799			
	0.2799	2.9347	$\bar{3}.0653$	2.324
0.0188	0.2771			
0.0188	0.2771			
	0.2771	2.9821	$\bar{3}.0179$	2.779
0.0125	0.2720			
0.0125	0.2720			
	0.2720	3.0684	$\bar{4}.9316$	3.417

Table 7
Neutral salt: 0.75 N KCl

Molality of $CuSO_4$	E.M.F.	pH	$\log C_H$	$x.10^2$
0.0500	0.2777			
0.0500	0.2777			
0.0500	0.2785			
	0.2780	2.9669	$\bar{3}.0331$	1.079
0.0375	0.2752			
0.0375	0.2753			
0.0375	0.2742			
0.0375	0.2742			
	0.2747	3.0227	$\bar{4}.9773$	1.265
0.0250	0.2707			
0.0250	0.2705			
0.0250	0.2704			
	0.2705	3.0937	$\bar{4}.9063$	1.612
0.0188	0.2683			
0.0188	0.2675			
	0.2679	3.1377	$\bar{4}.8623$	1.942
0.0125	0.2625			
0.0125	0.2625			
0.0125	0.2626			
0.0125	0.2624			
	0.2625	3.2291	$\bar{4}.7709$	2.360

Table 8
Neutral salt: 0.5 N KCl

Molality of $CuSO_4$	E.M.F.	pH	log C_H	$x.10^2$
0.0500	0.2654			
0.0500	0.2653			
	0.2654	3.1800	$\bar{4}.8200$	0.661
0.0375	0.2644			
0.0375	0.2645			
0.0375	0.2640			
0.0375	0.2639			
	0.2642	3.2004	4.7996	0.841
0.0250	0.2597			
0.0250	0.2597			
	0.2597	3.2764	$\bar{4}.7236$	1.058
0.0188	0.2575			
0.0188	0.2575			
	0.2575	3.1336	$\bar{4}.6864$	1.294
0.0125	0.2522			
0.0125	0.2522			
0.0125	0.2528			
0.0125	0.2527			
	0.2525	3.3982	$\bar{4}.6018$	1.599

Table 9
Neutral salt: 0.25 N KCl

Molality of $CuSO_4$	E.M.F.	pH	log C_H	$x.10^2$
0.0500	0.2500			
0.0500	0.2502			
	0.2501	3.4388	$\bar{4}.5612$	0.364
0.0375	0.2478			
0.0375	0.2478			
	0.2478	3.4777	$\bar{4}.5223$	0.444
0.0250	0.2441			
0.0250	0.2441			
	0.2441	3.5403	$\bar{4}.4597$	0.576
0.0188	0.2418			
0.0188	0.2419			
	0.2419	3.5775	$\bar{4}.4225$	0.706
0.0125	0.2373			
0.0125	0.2373			
	0.2373	3.6553	$\bar{4}.3447$	0.885

Table 10
Neutral salt: 1.0 N Na_2SO_4

Molality of $CuSO_4$	E.M.F.	pH	log C_H	$x \cdot 10^4$
0.0500	0.1896			
0.0500	0.1903			
	0.1900	4.4554	$\bar{5}.5446$	3.504
0.0375	0.1846			
0.0375	0.1846			
	0.1846	4.5468	$\bar{5}.4532$	3.785
0.0250	0.1790			
0.0250	0.1795			
	0.1793	4.6364	$\bar{5}.3636$	4.620
0.0188	0.1784			
0.0188	0.1785			
	0.1785	4.6499	$\bar{5}.3501$	5.972
0.0125	0.1744			
0.0125	0.1747			
	0.1746	4.7159	$\bar{5}.2841$	7.695

Table 11
Neutral salt: 0.50 N Na_2SO_4

Molality of $CuSO_4$	E.M.F.	pH	log C_H	$x \cdot 10^4$
0.0500	0.1925			
0.0500	0.1923			
	0.1924	4.4148	$\bar{5}.5852$	3.848
0.0375	0.1870			
0.0375	0.1870			
	0.1870	4.5061	$\bar{5}.4939$	4.157
0.0250	0.1839			
0.0250	0.1839			
	0.1839	4.5586	$\bar{5}.4414$	5.526
0.0188	0.1797			
0.0188	0.1799			
	0.1798	4.6280	$\bar{5}.3720$	6.281
0.0125	0.1784			
0.0125	0.1784			
	0.1784	4.6516	$\bar{5}.3484$	8.923

Table 12
Neutral salt: 0.50 N K_2SO_4

Molality of $CuSO_4$	E.M.F.	pH	log C_H	x.10^4
0.0500	0.1852			
0.0500	0.1854			
0.0500	0.1860			
	0.1855	4.5315	$\bar{5}$.4685	2.941
0.0375	0.1816			
0.0375	0.1820			
0.0375	0.1811			
	0.1816	4.5975	$\bar{5}$.4025	3.368
0.0250	0.1760			
0.0250	0.1766			
	0.1763	4.6872	$\bar{5}$.3128	4.110
0.0188	0.1676			
0.0188	0.1673			
0.0188	0.1680			
	0.1676	4.8342	$\bar{5}$.1658	3.907
0.0125	0.1630			
0.0125	0.1630			
	0.1630	4.9121	$\bar{5}$.0879	4.898

SUMMARY OF TABULATED RESULTS

Table 13

Degree of Hydrolysis of $CuSO_4$

Neutral salt: None

Molality of KCl	Molality of $CuSO_4$ (x.10^4)				
	0.0500	0.0375	0.0250	0.0188	0.0125
0.00	5.591	6.569	8.238	9.530	12.87

Table 14

Degree of Hydrolysis of $CuSO_4$

Neutral salt: KCl

Molality of KCl	Molality of $CuSO_4$ ($x \cdot 10^2$) 0.050	0.0375	0.0250	0.0188	0.0125
1.00	1.538	1.815	2.324	2.779	3.417
0.75	1.079	1.265	1.612	1.942	2.360
0.50	0.661	0.841	1.058	1.294	1.599
0.25	0.364	0.444	0.576	0.706	0.885

Table 15

Degree of Hydrolysis of $CuSO_4$

Neutral salt: NaCl

Molality of NaCl	Molality of $CuSO_4$ ($x \cdot 10^2$) 0.050	0.0375	0.0250	0.0188	0.0125
1.00	2.218	2.747	3.767	4.557	6.250
0.75	1.479	1.854	2.493	3.016	3.724
0.50	0.875	1.122	1.593	1.846	2.351
0.25	0.429	0.550	0.722	0.927	1.256

Table 16

Degree of Hydrolysis of $CuSO_4$

Neutral salt: K_2SO_4

Molality of K_2SO_4	Molality of $CuSO_4$ ($x \cdot 10^4$) 0.050	0.0375	0.0250	0.0188	0.0125
0.25	2.941	3.368	4.110	3.907	4.898

Table 17

Degree of Hydrolysis of $CuSO_4$

Neutral salt: Na_2SO_4

Molality of Na_2SO_4	Molality of $CuSO_4$ ($x \cdot 10^4$)				
	0.050	0.0375	0.0250	0.0188	0.0125
0.50	3.504	3.785	4.620	5.972	7.695
0.25	3.848	4.157	5.526	6.281	8.923

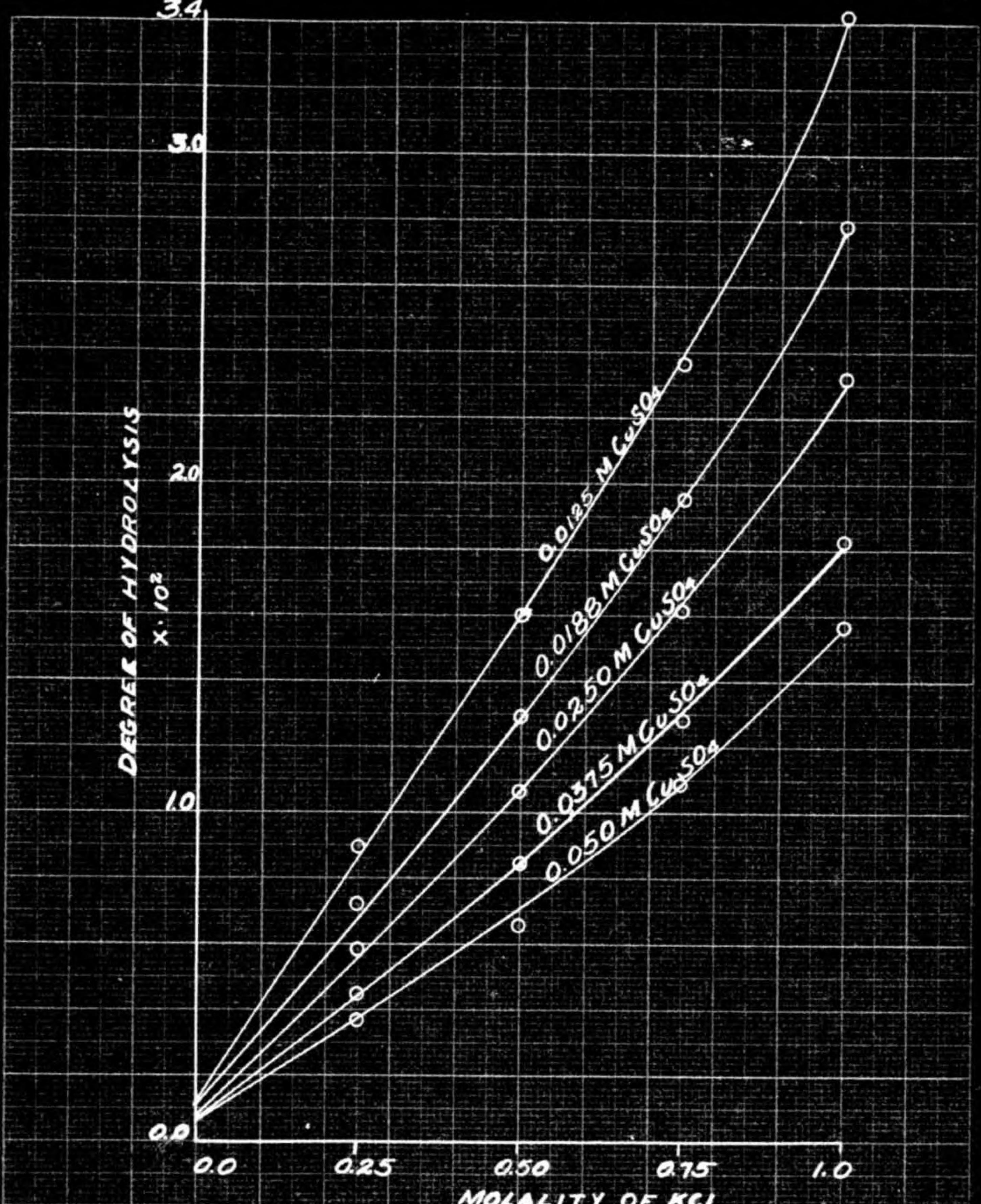
DEGREE OF HYDROLYSIS
X · 10²
3.4
3.0
2.0
1.0
0.0
0.0
0.25
0.50
0.75
1.0
MOLALITY OF KCl
0.0125 M CuSO4
0.0188 M CuSO4
0.0250 M CuSO4
0.0375 M CuSO4
0.050 M CuSO4

FIG. 1.

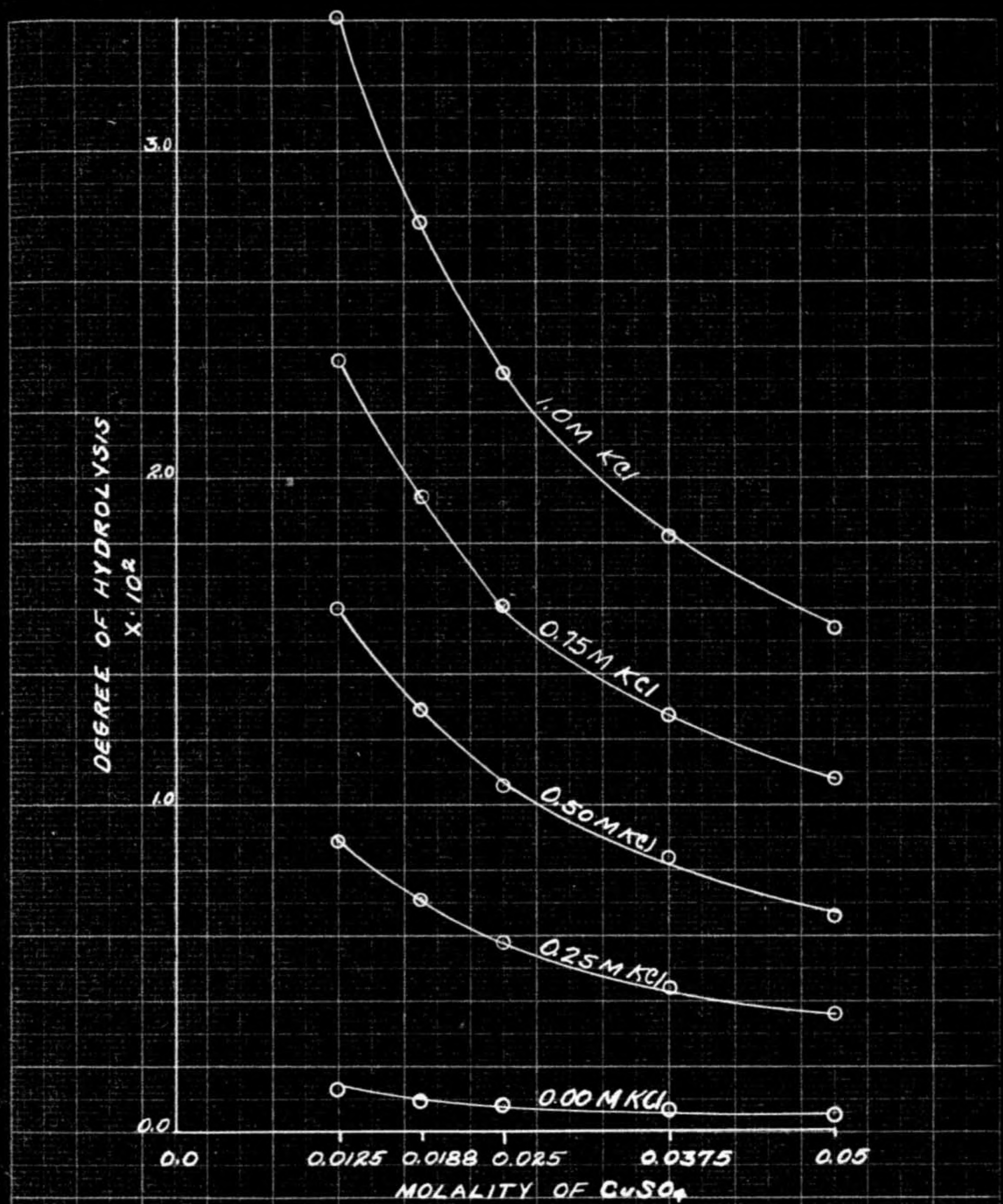
DEGREE OF HYDROLYSIS
X · 10²
3.0
2.0
1.0
0.0
1.0M KCl
0.75M KCl
0.50M KCl
0.25M KCl
0.00M KCl
0.0
0.0125
0.0188
0.025
0.0375
0.05
MOLALITY OF CuSO₄

FIG. 3.

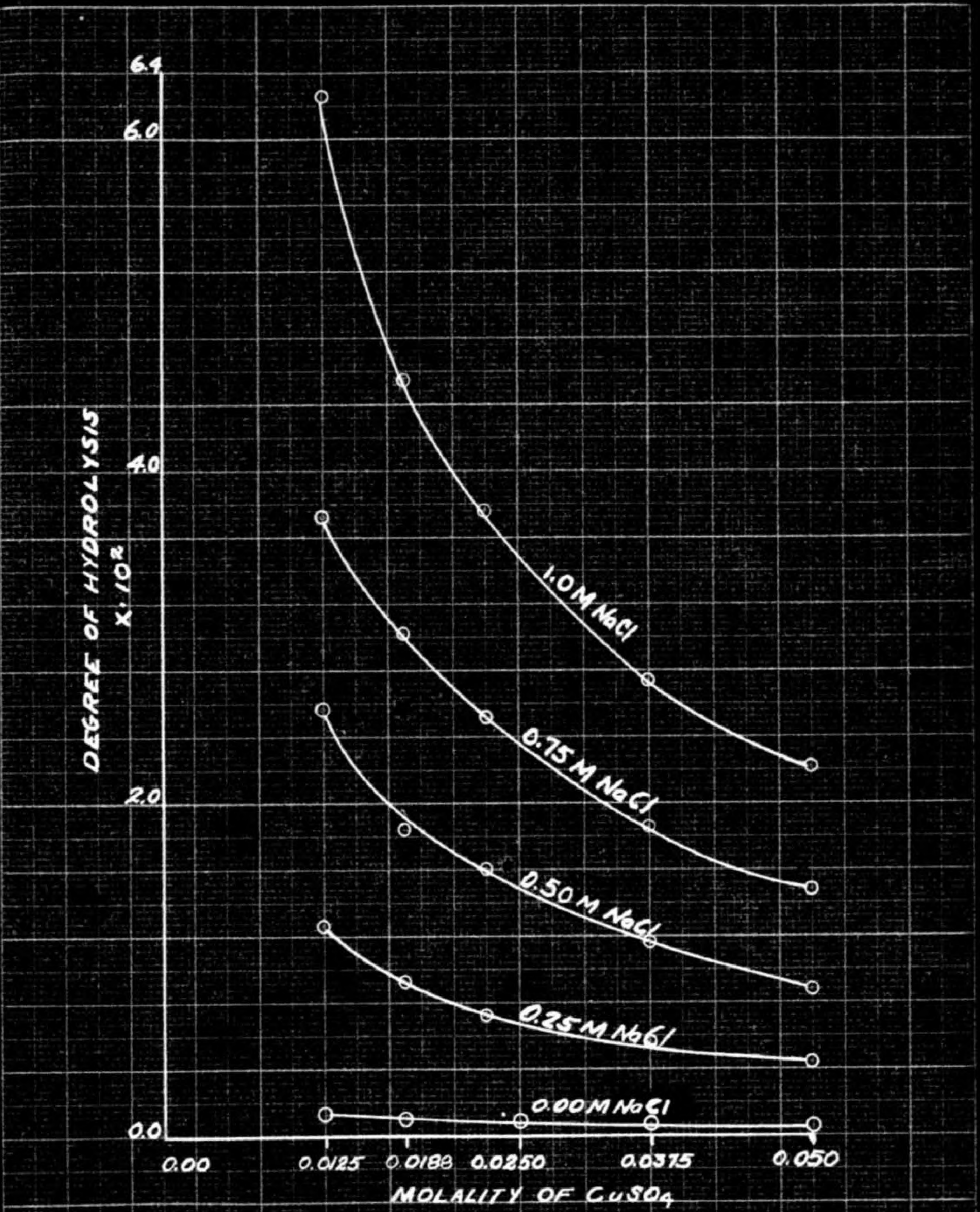
DEGREE OF HYDROLYSIS
X·10²
6.4
6.0
4.0
2.0
0.0
1.0 M NaCl
0.75 M NaCl
0.50 M NaCl
0.25 M NaCl
0.00 M NaCl
0.00
0.0125
0.0188
0.0250
0.0375
0.050
MOLALITY OF CuSO4

FIG. 4.

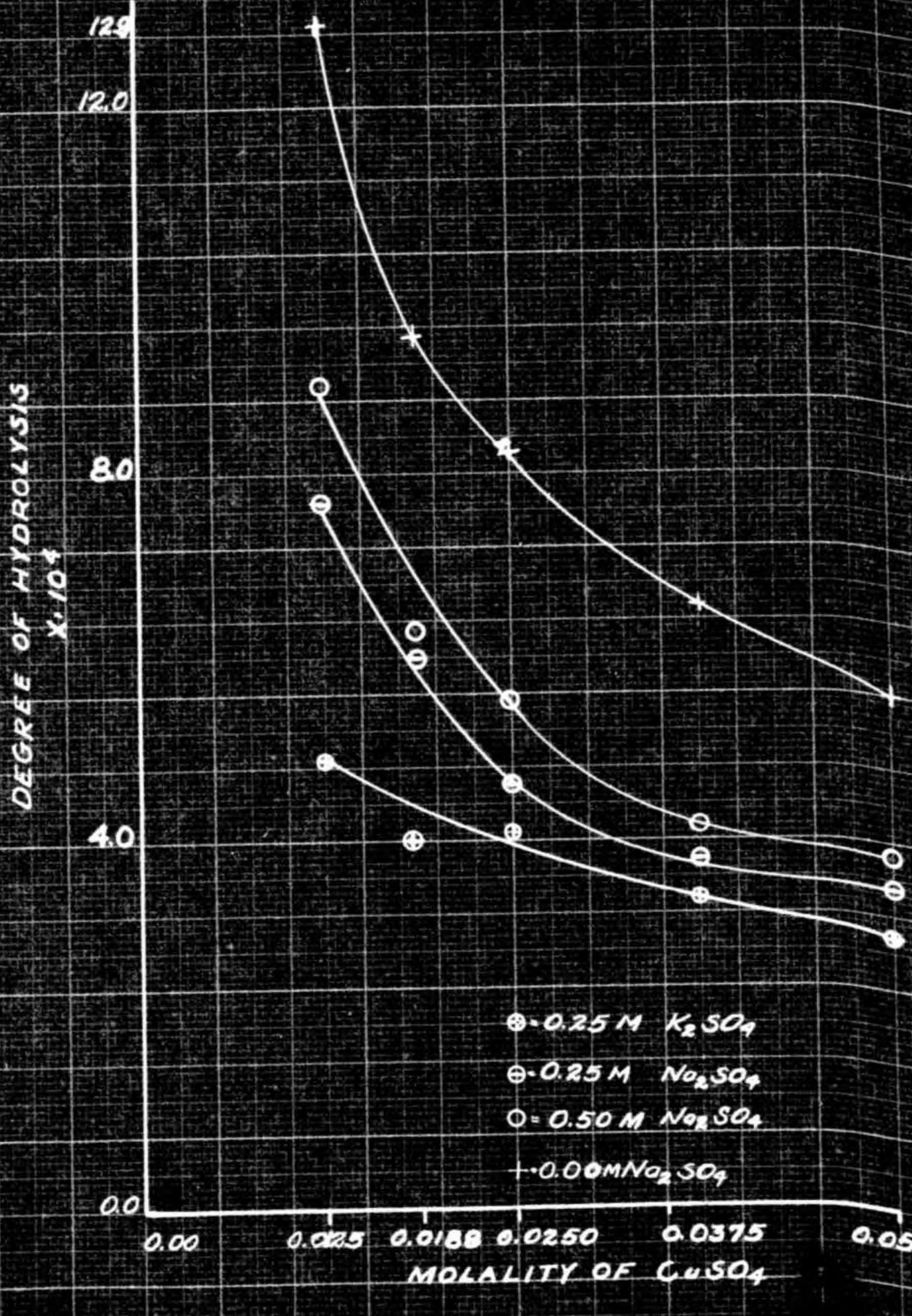
12.9
12.0
8.0
4.0
0.0
DEGREE OF HYDROLYSIS
X·10⁴
0.00
0.0125
0.0188
0.0250
0.0375
0.05
MOLALITY OF CuSO4
0.25 M K2SO4
0.25 M Na2SO4
0.50 M Na2SO4
0.00 M Na2SO4

FIG. 5

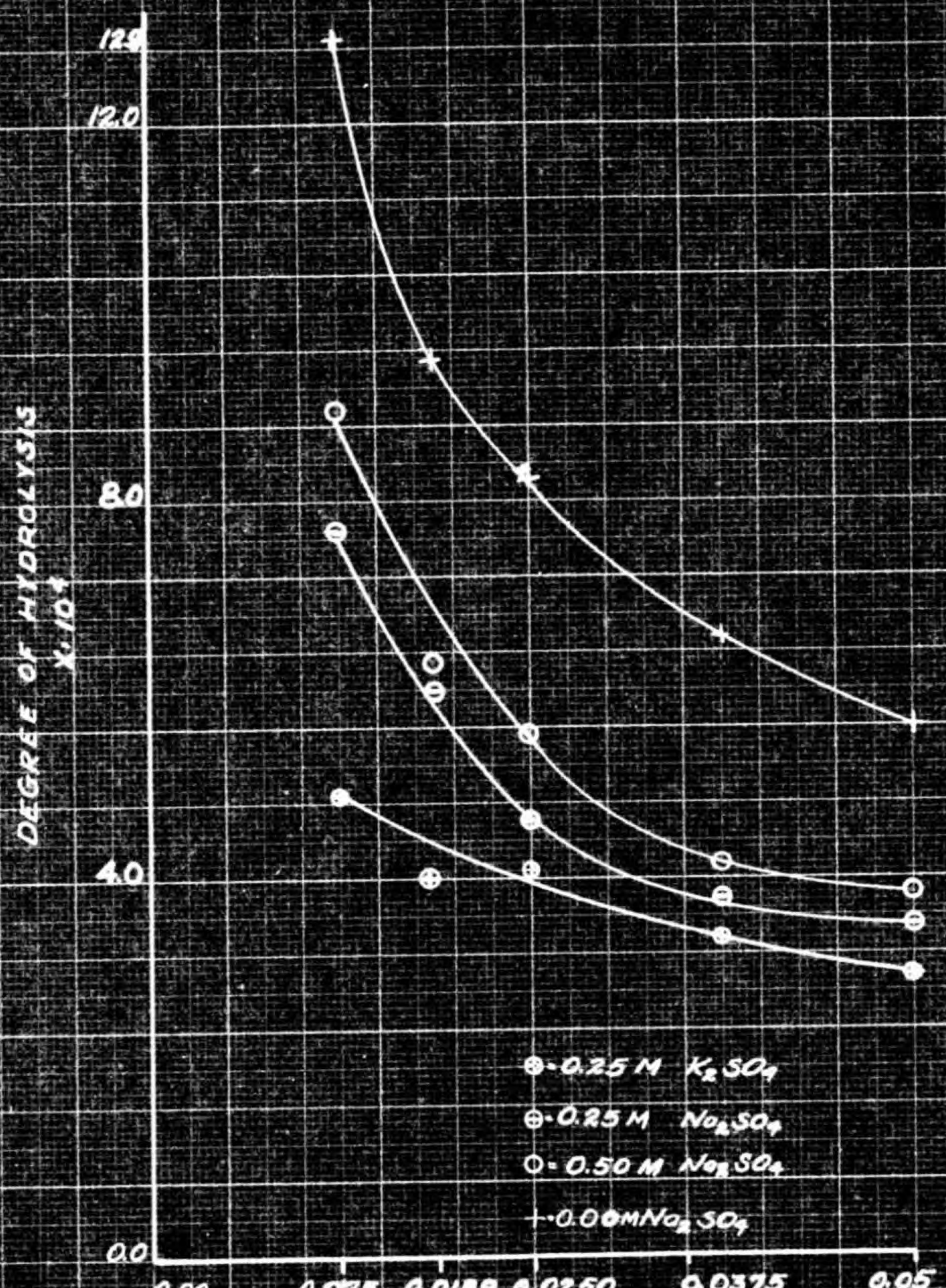
DEGREE OF HYDROLYSIS
X·10⁴
12.9
12.0
8.0
4.0
0.0
0.00
0.0125
0.0188
0.0250
0.0375
0.05
MOLALITY OF CuSO4
⊗-0.25 M K2SO4
⊕-0.25 M Na2SO4
O-0.50 M Na2SO4
+-0.00 M Na2SO4

FIG. 5